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**QUANTITATIVE NONDISPERSIVE X-RAY FLUORESCENCE
ANALYSIS OF HIGHLY RADIOACTIVE SAMPLES
FOR URANIUM AND PLUTONIUM CONCENTRATION**

August 14, 1973

Lawrence Livermore Laboratory
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Livermore, California

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ABSTRACT

Fluorescent x-ray energy spectra were successfully acquired from uranium and plutonium in 400:1 ratios in samples containing 2 Ci/gram of mixed fission products. The analytical system consists of a silver transmission anode x-ray tube, a low-Z scattering chamber, a magnetic β -ray trap, a beam monitor probe, a commercial Si(Li) detector, a set of modified electronics to handle the large γ -ray overload rate, and a computer analyzer using a higher-level language to handle data reduction.

The computer programs used to obtain peak areas from the closely spaced uranium and plutonium ($L\alpha_1 + 2$) peaks were constructed to make use of knowledge of upper-edge tailing gained in this experiment. Programs are being developed to properly remove background under the uranium and plutonium peaks. Absorption effects in the larger samples have been measured using the ratio of uranium ($L\beta$) to uranium ($L\gamma$) peak area and are incorporated in the data-analysis schemes. A titanium monitor probe, consisting of a fixed titanium plate near the sample, introduces a constant-area titanium K x-ray line into the spectrum. The program uses the area of this peak to correct for effects of total exciting flux, geometry, and system dead-time losses. Standard samples of various types are used to generate calibration curves from which quantitative results are obtained.

Samples are taken from dissolved high-burnup power-reactor fuel rods. The liquid sample is acidic and has a radiation level at one foot of approximately 2 R/hr β and 300 mR/hr γ . Sample

preparation involves only the evaporation of the liquid sample on a 1/2-mil polycarbonate substrate and subsequent sealing with another layer of polycarbonate film. The samples are then mounted in standard 35-mm slide-holders.

Preliminary testing on a limited number of prepared uranium and plutonium samples indicates a precision of about 1% and an accuracy of about 2%, over a range of 1 to 58 μg total mass. The samples have not yet been verified by independent chemical analysis. The system has been installed at the AEC Savannah River facility for extensive testing.

INTRODUCTION

The prototype nondispersive x-ray fluorescence system assembled and put into operation in a test and evaluation program at du Pont Savannah River Plant is intended to analyze "hot" dissolver solutions for elemental uranium and plutonium concentrations with a minimum of sample preparation and without the removal of the copious quantities of radioactive mixed fission products present. The solutions obtained by dissolving fuel rods from power reactors have uranium concentrations of about 50 g/liter, uranium to plutonium ratios ranging from 80 to 400, and radiation levels of about 2 Ci/g (β, γ).

SYSTEM DESCRIPTION

The system is made up of three parts: a movable unit (Fig. 1), referred to as the "X-ray data head," a computer analyzer, and a sample preparation stand.

The x-ray data head requires only 110 V AC power and a periodic liquid-nitrogen fill for the detector. It contains the tube-exciter system, the scattering chamber to hold the samples, a Si(Li) detector, and all the power supplies and electronics needed to produce the signal used for analysis. The following sections describe the subsystems that make up the X-ray data head. Figure 2 is a schematic drawing of the unit, and Figures 3, 4, and 5 are photographs for clarification of the description.

X-Ray Tube Exciter

The x-ray tube exciter is a pumpable, silver transmission anode of the air-cooled type, similar to that described by Jacklevic (1). This tube dissipates up to 50 W and delivers a flux of approximately 10^{10} photons/cm² per second at the sample (3-5 R/sec). The

Figure 1. X-ray data head, showing complete movable unit.

energy spectrum of the photon beam is shown in Fig. 6. The quality of the beam is expressed by the percent of the total flux in each of four regions. Region II contributes the major part of the Compton-scattered background under the peak used for analysis (uranium ($L\alpha$)). Regions III and IV are available for excitation of the sample, and comprise about 95% of the spectrum. The tube can be cycled up to air, have the target changed to another material, and be producing a useful x-ray beam in about 30 minutes. The tube is evacuated by a combination of a cryogenic molecular-sieve roughing pump, and an 8-liter/sec ion pump; the operating pressure is approximately 10^{-7} torr.

The photon beam can be varied by both the filament current and the grid cap bias. The beam flux has been measured to be stable and resettable to 1% (1 sigma),

The construction of this tube is difficult, but we have found it to be very reliable in operation.

Figure 2. Schematic drawing of equipment contained in the "x-ray data head" unit.

Figure 3. X-ray data head, front view.

Figure 4. X-ray data head, rear view.

Figure 5. X-ray data head, top view.

Figure 6. Energy spectrum of x-ray beam produced by the silver transmission anode tube; silver target 0.005 in. thick.

Scattering Chamber

The sample is held at 45 degrees to the exciting beam and to the detector by a plastic slide-holder. The chamber itself is made of aluminum, with lead shielding added to the outside for radiation protection of personnel.

Two sheets of titanium are placed on either side of the sample location so that the fluorescence from the titanium enters the detector directly. Figure 7 shows the scattering chamber, the plastic slide-holder, the titanium beam monitor sheets, and an actual sample, as seen through the beam dump port. An additional beam monitor can be inserted behind the sample to provide absorption information. The use of any beam monitor increases the Compton-scattering in the spectral region of interest, but its presence provides a normalization peak in each spectrum. The beam monitor is an "external standard" which completely removes the effect of fluctuations in beam fluence, all system dead-time corrections, pulse pile-up rejection losses, and changes in geometry.

The magnetic β -ray trap and the lead collimator (aluminum-lined) are located between the scattering chamber and the detector.

Figure 7. View of complete scattering chamber with sample and beam monitor as seen through the beam dump port.

Detector and Electronics

The system has been operated with Si(Li) detectors and electronic packages obtained from two different commercial sources. One detector is 10 mm² in area by 2 mm deep, while the other is 30 mm² by 3 mm deep. In both cases, the manufacturer developed special electronics packages to allow the systems to operate in the large flux of high-energy (100-keV to 3-MeV) γ -radiation from the sample. The γ -rays produce overload pulses in the detector. We find that the β -trap prevents any β -rays from reaching the detector, and the special electronics package allows the detector to operate in a γ -ray field of about 1 R/hr with only a 5% to 10% degradation in resolution. The detector resolution at 13.6 keV with the radioactive sample in the chamber is about 210 eV, FWHM.

The electronics package contains a preamplifier (pulsed-optical feedback), an amplifier with pulse pileup rejection and modifications for the overload gamma pulses, and high-voltage control and supply. A rate-meter was added to monitor the overall input count rate. Typical overload pulse rates are 3000 to 5000 cps, and the signal pulse rate is approximately the same.

Sample Preparation

The sample preparation equipment (Fig. 8) consists of a sintered stainless steel pellet which has a vacuum line attached. The vacuum line sucks a 0.5-mil polycarbonate sheet onto the slightly concave surface of the steel pellet. One 50-microliter drop of dissolver solution is placed on the film at the center and allowed to dry;

Figure 8. Sample preparation stand with heater control and polycarbonate film in place.

this takes a few minutes with the help of an infrared lamp or the heater element in the stand. After the sample is dry, adhesive is sprayed on the film and a second sheet of film is placed over the sample. This sandwich is then mounted in a standard 35-mm slide. Care must be taken to not allow large crystals to develop when the sample is drying, because they make an absorption correction necessary during analysis. We are currently exploring the use of freeze-drying techniques for an alternate method of sample preparation. Prefreezing of the sample before evaporation of the water prevents the formation of large single crystals.

Figure 9 shows some actual samples being inserted into the scattering chamber. The slide-holder is withdrawn for display. Note the radiation damage to the bottom of glass storage bottle in the foreground.

Analysis

Of the 104 α x-ray lines of uranium and plutonium, only the uranium ($L\alpha$ 1+2) and the plutonium ($L\alpha$ 1+2) are free from interference. The uranium ($L\alpha$) doublet is at about 13.613 keV and the plutonium ($L\alpha$) is at 14.279 keV, a difference of 666 eV. Figure 10 shows this part of a spectrum (uranium ($L\beta$), uranium ($L\alpha$), and plutonium ($L\alpha$) peaks) of an actual dissolver-solution sample. The uranium-plutonium ratio was 250:1 and the sample was highly radioactive. Figure 10 shows a similar spectrum from a sample containing

Figure 9. View of scattering chamber in use with various types of samples.

Figure 10. Actual energy spectra: (a) dissolver solution, U/Pu = 250; (b) uranium only, prepared standard; (c) log plot of complete spectrum of prepared standard (note titanium beam monitor peaks).

no plutonium or fission products; there is very little change in background or resolution. The primary analysis problem in using this data is to remove the upper tail of the large uranium (L α) peak from beneath the plutonium (L α). We are currently working on a technique which uses a double gaussian with upper and lower folded tails to represent the shape of the peaks in this region.

Figure 10 shows a typical spectrum in a log plot. Note the titanium beam monitor peak and the uranium (L α) peak. The net peak areas of these two peaks are obtained with linear background subtraction routines that use clear areas above and below the peaks. The uranium (L α) peak area is then divided by the titanium (K α + β) peak area and multiplied by a constant.

We have begun extensive calibration experiments both at LLL and du Pont Savannah River. Initially, we used prepared standards with known quantities of uranium ranging from 1 to 100 μ g, with no fission products.

Our tests at LLL have resulted in a measured reproducibility for a particular sample of 0.2% (1 sigma) and a variance between samples of supposedly equal masses of 0.6% (1 sigma). We have not yet been able to check our standards by an independent method.

The data analysis takes approximately 30 seconds and the typical acquisition time is about 10 minutes. Our reproducibility checks showed no dependence on count rate, on sample position, or on uranium amounts, to within 0.2% (1 sigma). With the prepared standards we have measured the linearity of the system for uranium mass to be 1% (1 sigma) from 1 μ g to 58.1 μ g total uranium mass.

We are greatly encouraged by these results and are looking forward to using the sets of standards now being made at du Pont Savannah River. These standards will contain the complete inventory of fission products and will have various ratios of uranium to plutonium.

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